



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

re application of:

**Youichi TEI *et al.***

Application No. 10/706,987

**Confirmation No. 7491**

Filed: November 14, 2003

For: THERMOPLASTIC  
ALLYLOXYMETHYLSTYRENE-  
BASED RESIN

Art Unit: 1796

Examiner: Helen L. Pezzuto

Atty. Docket No. 32307-192751

Customer No.

**26694**

PATENT TRADEMARK OFFICE

**TRANSMITTAL OF CERTIFIED TRANSLATION OF PRIORITY DOCUMENT**

Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

Sir:

This paper is filed in view of a telephone request from the Examiner on or about November 28, 2007 during which the Examiner requested a certified translation of the 35 USC §119 priority document.

Enclosed is a certified translation of the priority document JP 2002-331197, filed November 14, 2002. Benefit of priority of the priority document was claimed on November 14, 2003 in the instant U.S. application.

This paper is filed concurrently with the Issue Fee Payment.

Respectfully submitted,

Dated:

June 3 2008

Marina V. Schneller

Marina V. Schneller

Registration No. 26,032

VENABLE LLP

P.O. Box 34385

Washington, D.C. 20043-9998

Telephone: (202) 344-4000

Telefax: (202) 344-8300

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Group Art unit: 1796  
Examiner: Helen L. Pezzuto

Applicants : Youichi TEI et al. )  
Application No. : 10/706,987 ) TRANSLATION OF  
Filed : November 14, 2003 ) PRIORITY DOCUMENTS  
For : THERMOPLASTIC ) AND DECLARATION IN  
ALLYLOXYMETHYLSTYRENE-BASED ) SUPPORT THEREOF  
RESIN )

Assistant Commissioner for Patents  
Washington, D.C. 20231

Sir:

I, Atsuko SEKIGUCHI, of Tani & Abe Patent Office, No. 6-20, Akasaka 2-chome, Minato-ku, Tokyo 107-0052, Japan, declare that:

1. I know well both the Japanese and English languages.
2. I translated Japanese Patent Application No.2002-331197 of November 14, 2002 from the Japanese language to the English language, a copy of the translation being attached hereto.
3. The attached English translation of the Japanese application identified in paragraph 2 above is a true and correct translation to the best of my knowledge and belief.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Signed this 14th day of December, 2007

Atsuko Sekiguchi  
Atsuko SEKIGUCHI

PATENT OFFICE  
JAPANESE GOVERNMENT

This is to certify that the annexed is a true copy of the following application as filed with this Office.

Date of Application: November 14, 2002

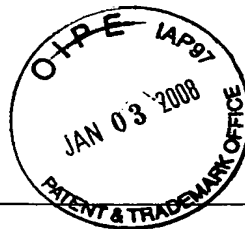
Application Number: Japanese Patent Application  
No. 2002-331197

Applicant(s): FUJI ELECTRIC DEVICE TECHNOLOGY CO., LTD.  
Toshiyuki KODAIRA

March 17, 2004

Commissioner,  
Patent Office Yasuo IMAI

Certificate No. 2003-3109911



(Translation)  
No. 2002-331197

(1/2)

(Document Name) Patent Application

(Case Number) 02P01459

(Filing Date) November 14, 2002

To: Commissioner, the Patent Office

(International Patent Classification) C08F 12/00

(Title of the Invention) A THERMOPLASTIC  
ALLYLOXYMETHYLSTYRENE-BASED RESIN

(Number of claims) 12

(Inventor)

Address: c/o Fukui University  
9-1 Bunkyo 3-chome, Fukui-shi, Fukui

Name: Toshiyuki KODAIRA

(Inventor)

Address: c/o Fuji Electric Co., Ltd.  
1-1, Tanabeshinden, Kawasaki-ku,  
Kawasaki-shi, Kanagawa

Name: Youichi TEI

(Applicant)

Identification Number: 000005234

Name: Fuji Electric Co., Ltd.

(Applicant)

Address: c/o Fukui University  
9-1 Bunkyo 3-chome, Fukui-shi, Fukui

Name: Toshiyuki KODAIRA

(Agent)

(2/2)

(Identification Number) 100077481

(Patent Attorney)

(Name) Yoshikazu TANI

(Appointed Agent)

(Identification Number) 100088915

(Patent Attorney)

(Name) Kazuo ABE

(Appointed Agent)

(Identification Number) 100106998

(Patent Attorney)

(Name) Denichi HASHIMOTO

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(Necessity of Proof) Yes



[DOCUMENT NAME] SPECIFICATION

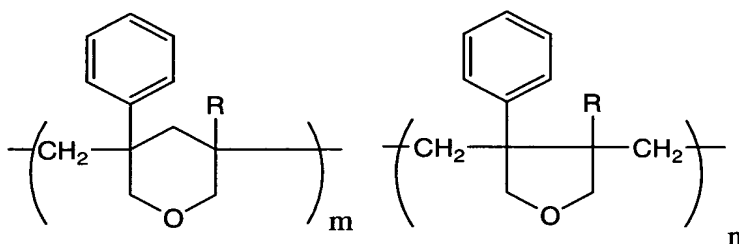
[TITLE OF THE INVENTION] A THERMOPLASTIC  
ALLYLOXYMETHYLSTYRENE-BASED RESIN

[SCOPE OF CLAIM FOR A PATENT]

5 [Claim 1]

A thermoplastic allyloxymethylstyrene-based resin comprising structural units of the following formulas (I) and (II):

[Chemical Formula 1]



(I)

(II)

10

as repeating units, wherein R represents a hydrogen atom or a hydrocarbon group, and m and n each denote an integer of 0 or 1 or higher, provided that m and n are not 0 at the same time.

15 [Claim 2]

The thermoplastic resin according to claim 1, wherein R is phenyl.

[Claim 3]

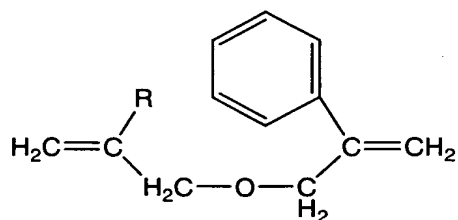
20 The thermoplastic resin according to claim 1, wherein R is hydrogen.

[Claim 4]

A thermoplastic resin obtained by

polymerizing a monomer having a structure of the following formula (III):

[Chemical Formula 2]



(III)

5 wherein R represents a hydrogen atom or a hydrocarbon group.

[Claim 5]

The thermoplastic resin according to claim 4, wherein R is phenyl.

10 [Claim 6]

The thermoplastic resin according to claim 4, wherein R is hydrogen.

[Claim 7]

15 The thermoplastic resin according to claim 5 which has a degree of cyclization of 90% or higher.

[Claim 8]

20 The thermoplastic resin according to claim 6 which has a degree of cyclization of 80% or higher.

[Claim 9]

The thermoplastic resin according to claim



5 which has a glass transition temperature (Tg) of 180 °C or higher, but lower than 270 °C.

[Claim 10]

5 The thermoplastic resin according to claim 6 which has a glass transition temperature (Tg) of 100 °C or higher, but lower than 125 °C.

[Claim 11]

The thermoplastic resin according to any one of claims 4 to 6 which has a thermal  
10 decomposition point of 350 °C or higher.

[Claim 12]

The thermoplastic resin according to any one of claims 4 to 6 which has a moisture content of less than 0.01%.

15 [DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Technical Field to Which the Invention Pertains]

This invention relates to allyloxymethylstyrene-based resin. In particular,  
20 this invention relates to a phenylallyloxymethylstyrene resin and an allyloxymethylstyrene resin, which are composed of repeating structural units derived from a phenylallyloxymethylstyrene monomer and an  
25 allyloxymethylstyrene monomer, respectively, and which have excellent heat resistance, humidity resistance and moldability, and to a method for

production thereof.

[0002]

[Prior Art]

Thermoplastic resins are used as molding  
5 materials in a wide range, including electric and  
electronic component materials and medical care  
materials. With the progress of technologies, a  
demand for products with higher performance and  
higher characteristics such as reliability is  
10 growing. Accordingly, the presence of  
thermoplastic resins with higher resistance to  
heat and humidity is desired.

[0003]

So far, materials using polymethacrylate  
15 resins (PMMA) and polycarbonate resins (PC) (see,  
for example, Patent Literature 1) have been known  
as polymeric materials for optical use or for  
recording media. Although polymethacrylate resins  
and polycarbonate resins are excellent in  
20 transparency, those are problematical in heat  
resistance and humidity resistance.

[0004]

In recent years, there are disclosed  
norbornene-based polyolefin resins as polymeric  
25 materials improved in these drawbacks (see, for  
example, Patent Literature 2, 3 and 4), and show  
that these resins have relatively good properties,

such as heat resistance and humidity resistance,  
in comparison with PMMA and PC.

[0005]

[Patent Literature 1]

5 Japanese Patent Application Laid-open No.  
2000-153535

[0006]

[Patent Literature 2]

Japanese Patent Application Laid-open No.  
10 Hei 7-153060

[0007]

[Patent Literature 3]

Japanese Patent Application Laid-open No. Hei  
7-210855

15 [0008]

[Patent Literature 4]

Japanese Patent Application Laid-open No.  
Hei 9-85743

[0009]

20 [Problems to Be Solved by the Invention]

However, the existing polymeric materials  
are still insufficient in satisfying stricter  
performance requirements imposed in recent years,  
including higher performance and higher

25 reliability.

[0010]

It is an object of the present invention to

provide a high-performance polymeric material having higher stability to heat and lower hygroscopicity.

[0011]

5 [Means for Solving the Problems]

The above-described problems can be solved by using a polymeric material retaining an appropriate molecular structure and appropriate physical properties and a molded article obtained  
10 under appropriate molding conditions. The appropriate structure herein refers to a rigid three-dimensional stereochemical structure such as a cyclic structure. The appropriate physical properties refer to a high glass transition point  
15 (high T<sub>g</sub>) closely related to mechanical strength characteristics, high thermal stability (high thermal decomposition temperature) permitting high flow molding, and low hygroscopicity (minimal swelling, deformation or deterioration due to  
20 moisture absorption). The appropriate molding conditions refer to high flow molding conditions which suppress the occurrence of residual stress of the resulting molded article and ensure its high surface accuracy.

25 [0012]

More specifically, the use of a thermoplastic allyloxymethylstyrene-based resin,

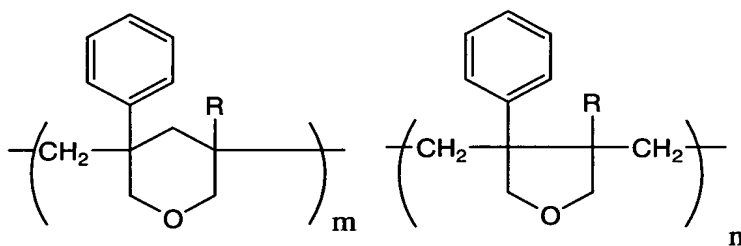
which is a completely novel polymeric material having all of the above-mentioned physical properties, makes it possible to achieve a high resin melt temperature, permit the material to be  
5 molded at a high mold temperature and solve the problems.

[0013]

That is, according to a first aspect of the present invention is a thermoplastic  
10 allyloxymethylstyrene-based resin comprising structural units of the following formulas (I) and (II):

[0014]

[Chemical Formula 3]



(I)

(II)

15 as repeating units, wherein R represents a hydrogen atom or a hydrocarbon group, and m and n each denotes an integer of 0 or 1 or higher, provided that m and n are not 0 at the same time.

20 [0015]

According to a second aspect of the present invention, in the thermoplastic

allyloxymethylstyrene-based resin, R in the formulas (I) and (II) is phenyl.

[0016]

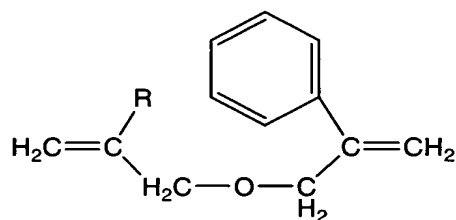
According to a third aspect of the present invention, in the thermoplastic allyloxymethylstyrene-based resin, R in the formulas (I) and (II) is hydrogen.

[0017]

According to a fourth aspect of the present invention, the thermoplastic resin is obtained by polymerizing a monomer having a structure of the following formula (III):

[0018]

[Chemical Formula 4]



(III)

[0019]

wherein R represents a hydrogen atom or a hydrocarbon group.

[0020]

According to a fifth aspect of the present invention, in the thermoplastic resin, R is phenyl in the formula (III).

[0021]

According to a sixth aspect of the present invention, in the thermoplastic resin, R is hydrogen in the formula (III).

5 [0022]

According to a seventh aspect of the present invention, in the case where in the thermoplastic resin, R is phenyl in the formula (III), a degree of cyclization of 90% or higher.

10 [0023]

According to an eighth aspect of the present invention, in the case where in the thermoplastic resin, R is hydrogen in the formula (III), a degree of cyclization of 80% or higher.

15 [0024]

According to a ninth aspect of the present invention, in the case where in the thermoplastic resin, R is phenyl in the formula (III), a glass transition temperature (T<sub>g</sub>) is 180 °C or higher, but lower than 270 °C.

[0025]

According to a tenth aspect of the present invention, in the case where in the thermoplastic resin, R is hydrogen in the formula (III), a glass transition temperature (T<sub>g</sub>) is 100 °C or higher, but lower than 125 °C.

[0026]





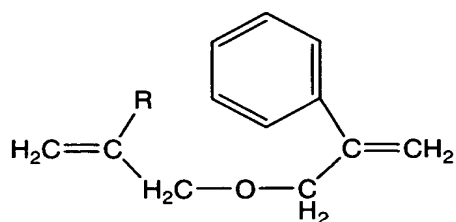
but not limited to, alkyl groups such as methyl and ethyl, cycloalkyl groups such as cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl, aryl groups such as phenyl and naphthyl, and aromatic  
5 heterocyclic groups such as pyridyl and furyl.  
[0031]

Preferably, R is hydrogen or phenyl.  
[0032]

The phenyl groups in the formulas (I) and  
10 (II) may be optionally substituted, as long as the effects of the present invention are exhibited. Examples of the substituents in this case are lower alkyl groups such as methyl and ethyl.  
[0033]

15 Next, an outline of the method for synthesizing the thermoplastic allyloxymethylstyrene-based resin will be offered.  
[0034]

The thermoplastic allyloxymethylstyrene-  
20 based resin of the present invention is obtained by polymerizing a monomer having a structure of the following formula (III):  
[0035]  
[Chemical Formula 6]



(III)

[0036]

wherein R represents a hydrogen atom or a hydrocarbon group.

5 [0037]

Examples of the hydrocarbon group as R are, but not limited to, alkyl groups such as methyl and ethyl, cycloalkyl groups such as cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl, aryl groups such as phenyl and naphthyl, and aromatic heterocyclic groups such as pyridyl and furyl.

[0038]

Preferably, R is hydrogen or phenyl.

[0039]

15 The phenyl group in the formula (III) may be optionally substituted, as long as the effects of the present invention are exhibited. Examples of the substituent in this case are lower alkyl groups such as methyl and ethyl.

20 [0040]

The method of synthesizing the phenylallyloxymethylstyrene resin and the

allyloxymethylstyrene resin will be briefly described as specific examples.

[0041]

As the method for synthesizing the phenylallyloxymethylstyrene resin, an explanation will be offered for a method which comprises synthesizing phenylallyloxymethylstyrene monomer and polymerizing the monomer.

[0042]

Phenylallyloxymethylstyrene monomer can be obtained by mixing tetranormalbutylammonium bromide, as a phase transfer catalyst, for example, with 2 parts by weight of  $\alpha$ -hydroxymethylstyrene and 1 part by weight of  $\alpha$ -bromomethylstyrene, and reacting the mixture for 50 hours or more at a constant temperature in basicity. From the resulting product, phenylallyloxymethylstyrene monomer is isolated and purified.

[0043]

Then, a predetermined amount of the phenylallyloxymethylstyrene monomer obtained by the above method, and a polymerization initiator such as 2,2'-azobisisobutyronitrile or cumene hydroperoxide are mixed into a polymerization tube. The tube is sealed in an atmosphere of nitrogen, or after a freeze-pump-thaw cycle is repeated several times for a predetermined time, the tube

is sealed in a vacuum. Then, the reaction mixture is allowed to stand for several hours at a predetermined temperature to carry out polymerization. Then, the reaction mixture is  
5 rapidly cooled to give a thermoplastic phenylallyloxymethylstyrene resin.

[0044]

Next, a method, which comprises synthesizing allyloxymethylstyrene monomer and  
10 polymerizing the monomer, will be described as the method for synthesizing the allyloxymethylstyrene resin.

[0045]

Allyloxymethylstyrene monomer can be  
15 obtained by mixing, for example, 0.5 part by weight of tetranormalbutylammonium bromide, as a phase transfer catalyst, with 1 part by weight of  $\alpha$ -hydroxymethylstyrene and 10 parts by weight of allyl bromide, and reacting the mixture for 50  
20 hours or more at a constant temperature in basicity. From the resulting product, allyloxymethylstyrene monomer is isolated and purified.

[0046]

25 Then, a predetermined amount of the allyloxymethylstyrene monomer obtained by the above method, and a polymerization initiator such

as 2,2'-azobisisobutyronitrile or cumene hydroperoxide are mixed into a polymerization tube. The tube is sealed in an atmosphere of nitrogen, or after a freeze-pump-thaw cycle is repeated  
5 several times for a predetermined time, the tube is sealed in a vacuum. Then, the reaction mixture is allowed to stand for several hours at a predetermined temperature to carry out polymerization. Then, the reaction mixture is  
10 rapidly cooled to give a thermoplastic allyloxymethylstyrene resin.

[0047]

Examples of the phase transfer catalyst, other than the above-mentioned  
15 tetranormalbutylammonium bromide, are, but not limited to, tetranormalbutylammonium chloride, crown ether + KCl, and crown ether + KBr.

[0048]

Examples of the polymerization initiator  
20 are, but not limited to, azo compounds, other than the above-mentioned 2,2'-azobisisobutyronitrile, such as 2,2'-azobis-2-methylbutyronitrile, 2,2'-azobis-2-methylvaleronitrile, 2,2'-azobis-2,3-dimethylbutyronitrile, 2,2'-azobis-2-  
25 methylhexanenitrile, 2,2'-azobis-2,4-dimethylvaleronitrile, 2,2'-azobis-2,3,3-trimethylbutyronitrile, 2,2'-azobis-2-

methylheptanenitrile, 2,2'-azobis-2-cyclopropylpropionitrile, 2,2'-azobis-2-cyclopentylpropionitrile, 2,2'-azobis-2-benzylpropionitrile, 2,2'-azobis-2-(4-nitrobenzyl)propionitrile, 2,2'-azobis-2-cyclobutylpropionitrile, 2,2'-azobis-2-cyclohexylpropionitrile, 2,2'-azobis-2-(4-chlorobenzyl)propionitrile, 2,2'-azobis-2-ethyl-3-methylvaleronitrile, 2,2'-azobis-2-isopropyl-3-methylvaleronitrile, 2,2'-azobis-2-isobutyl-4-methylvaleronitrile, 1,1'-azobis-1-cyclohexanenitrile, 1,1'-azobis-1-cyclobutanenitrile, 2,2'-azobis-2-carbomethoxypropionitrile, and 2,2'-azobis-2-carboethoxypropionitrile; and peroxides, other than the aforementioned cumene hydroperoxide, such as methyl ethyl ketone peroxide, cyclohexanone peroxide, bis-(1-oxycyclohexyl) peroxide, acetyl peroxide, capryl peroxide, lauroyl peroxide, stearoyl peroxide, benzoyl peroxide, p,p'-dichloro-benzoyl peroxide, (2,4,2',4'-tetrachloro)-benzoyl peroxide, di-t-butyl peroxide, di-t-amyl peroxide, t-butyl-cumyl peroxide, dicumyl peroxide, 2,5-dimethyl-2,5-di(t-butyl peroxide)-hexane, t-butyl hydroperoxide, p-menthane hydroperoxide, 2,5-dimethyl-2,5-dihydroperoxide-hexane, t-butyl peracetate, t-

butyl perisobutyrate, t-butyl perpivalate, t-butyl perbenzoate, di-t-butyl perphthalate, 2,5-dimethyl(2,5-benzoylperoxy)-hexane, t-butyl permaleate, i-propyl percarbonate, t-butylperoxy-  
5 i-propyl carbonate, and succinic acid peroxide.  
[0049]

The degree of cyclization for the thermoplastic allyloxymethylstyrene-based resin can be controlled according to the type and the  
10 amount of addition of the polymerization initiator, and further the polymerization temperature or the polymerization time. To retain the predetermined glass transition point (T<sub>g</sub>) and heat stability as a thermoplastic resin, the degree of cyclization  
15 of the resulting thermoplastic phenylallyloxymethylstyrene resin needs to be 90% or higher, more desirably 99% or higher, while the degree of cyclization of the resulting thermoplastic allyloxymethylstyrene resin needs to  
20 be 80% or higher, more desirably 88% or higher.  
[0050]

The degree of cyclization is determined by the ratio between a cyclic  
phenylallyloxymethylstyrene unit or a cyclic  
25 allyloxymethylstyrene unit and a pendant olefin structure in polymers that are obtained by NMR (nuclear magnetic resonance) measurement.

[0051]

If the degree of cyclization of the thermoplastic allyloxymethylstyrene-based resin is low, this means that many pendant olefin structural moieties, which have not been cyclized, are present in the repeating units of the polymer. As a result, there will be a decrease in the molecular weight, and declines in the glass transition point (Tg) and heat stability as a thermoplastic resin. Eventually, the drawbacks occur that the mechanical strength, thermal stability, shape stability and predetermined surface accuracy as an injection molded article fail to be obtained.

[0052]

The glass transition point (Tg) of the thermoplastic allyloxymethylstyrene-based resin is obtained by thermomechanical analysis (TMA) or differential scanning calorimetry (DSC). With DSC, for example, Tg is measured within the temperature range of -50 °C to 300 °C at a heating rate of 5 °C/min.

[0053]

The glass transition point (Tg) of the thermoplastic allyloxymethylstyrene-based resin varies with the molecular weight or the degree of cyclization, and Tg is 100 °C or higher at a



degree of cyclization of 80% or higher.

Specifically, the thermoplastic

phenylallyloxymethylstyrene resin controlled with  
a degree of cyclization of 90% or higher, has 180

5 °C < Tg < 270 °C, preferably 200 °C < Tg < 270 °C.

The thermoplastic allyloxymethylstyrene resin

controlled with a degree of cyclization of 88% or  
higher, has Tg of 100 °C or higher. A molded

article, which is obtained by injection molding

10 the thermoplastic phenylallyloxymethylstyrene

resin or the thermoplastic allyloxymethylstyrene

resin with the glass transition point within this

range can retain sufficient mechanical strength,

heat stability, shape stability and predetermined

15 surface accuracy.

[0054]

The molecular weight (Mn) of the

thermoplastic allyloxymethylstyrene-based resin is  
preferably 1,500 to 30,000, more preferably 2,000

20 to 25,000, even more preferably 3,000 to 20,000.

[0055]

The heat stability of the thermoplastic

allyloxymethylstyrene-based resin is determined by  
thermogravimetric analysis (TG). For this

25 determination, a thermogravimetric analyzer

("TG/DTA220", Seiko Instruments Inc., Japan) is

used, and the temperature at which a weight loss

of 0.5% occurs under heat, is determined as a thermal decomposition point under the conditions of a sample amount of  $5 \text{ mg} \pm 0.5$ , an  $\text{N}_2$  flow rate of 200 ml/min, a measurement temperature of 30 to 5 600 °C, and a heating temperature of 10 °C/min. [0056]

The thermal decomposition point of the thermoplastic allyloxymethylstyrene-based resin also varies with the aforementioned degree of 10 cyclization, etc., and is preferably 350°C or higher. Specifically, the thermoplastic phenylallyloxymethylstyrene resin controlled with a degree of cyclization of 90% or higher, has the thermal decomposition point of 360°C or higher. 15 The thermoplastic allyloxymethylstyrene resin controlled with a degree of cyclization of 88% or higher, has the thermal decomposition point of 350°C or higher. Even in high-temperature melt state during injection molding, deterioration of 20 the low molecular weight components inferior in heat stability does not occur. Consequently, no defects measuring several micrometers to several tens of micrometers are produced on the surface of the injection molded product, which can retain 25 sufficient surface accuracy. [0057]

The moisture content of the thermoplastic

allyloxymethylstyrene-based resin is determined by Karl Fischer analysis or thermal desorption mass spectrometry (TDS). With TDS, for example, the moisture content can be determined by measuring  
5 H<sub>2</sub>O gas (M/Z = 18), which is generated during resin melt at 30 °C to 400 °C in a vacuum at a heating rate of 5 °C/min, by a quadruple mass spectrometer.

[0058]

10           The moisture content of the thermoplastic allyloxymethylstyrene-based resin depends greatly on the chemical structure of this resin. That is, there are no polar functional groups in the structural units, and stereostructures, such as a  
15 cyclic phenylallyloxymethylstyrene structure and a cyclic allyloxymethylstyrene structure, are polymerized in the resin. These features result in low hygroscopicity, which is reflected in the moisture content. A moisture content of 0.01% or  
20 less can be retained by the thermoplastic phenylallyloxymethylstyrene resin and the thermoplastic allyloxymethylstyrene resin having a structure, a formula and physical properties controlled to achieve the aforementioned degree of  
25 cyclization and thermal decomposition temperature. As a result, a molded article obtained by injection molding can be a product with high

environmental reliability which shows no morphological changes associated with moisture absorption, for example, in environmental stability tests allowing the molded article to stand under high temperature, high humidity conditions, or which shows no defects on the surface of the molded article in condensation formation tests involving transfer from high temperature, high humidity conditions to low temperature, low humidity conditions.

[0059]

The thermoplastic allyloxymethylstyrene-based resin of the present invention can be molded by a well-known molding method, such as injection molding, extrusion, inflation molding, blow molding, injection blow molding, press molding, rotational molding, cutting molding, vacuum molding, rolling, cast molding, or calendaring.

[0060]

In molding the thermoplastic allyloxymethylstyrene-based resin of the present invention, the following substances may be incorporated with the aim of improving the physical properties such as moldability, charging properties, melt flow characteristics, mechanical strength, flexibility, impact resistance, adhesion of a coating agent, weather resistance, humidity

resistance, light blocking properties, fire retardancy, creep resistance, surface hardness, thermal expansibility, and elasticity: antioxidants such as phenolic or phosphorus-based compounds; ultraviolet stabilizers such as benzophenones or hindered amines; antistatic agents such as amines; lubricants such as esters of aliphatic alcohols; plasticizers such as phthalates; additives such as dyes, pigments, flame retardants and slip agents; fine particulate fillers such as silica, alumina, talc, aluminum hydroxide, carbon, amorphous carbon, graphite, and calcium carbonate; and fibrous fillers such as glass fiber, carbon fiber, boron fiber, silicon carbide fiber, asbestos fiber, potassium titanate crystal fine fiber, quartz fiber, metallic fiber, carbon fibril, polyamide fiber, polyester fiber, fluoroplastics fiber, cotton fiber, cellulose fiber, and silicon fiber.

[0061]

Other resins can be mixed unless the objects of the present invention are impaired. For example, norbornene-based polyolefin resins, polycarbonate resins, and polymethyl methacrylate resins can be mixed.

[0062]

The thermoplastic allyloxymethylstyrene-

based resin of the present invention is useful as various molded articles in wide varieties of fields, including substrate materials for optical and magnetic media. Examples include electric and electronic components, such as optical disks, information disks, magnetic disks, hard disks, optical cards, and electrophotographic photoconductors, optical components, such as optical lenses, eyeglass lenses, prisms, optical mirrors, optical fibers, beam splitters, liquid crystal display device substrates, light-guiding plates, polarization films, phase difference films, OHP films, light diffusion plates, light emitting device encapsulated light diffusion plates, back lights for liquid crystal, and pipe materials for fluorescent tubes; equipments for medical care, for example, containers for liquid or solid pharmaceuticals, such as chemical liquid containers, vials, ampules, pre-filled syringes, infusion bags, containers for solid drugs, containers for eye drops, containers for contrast media, and press-through packages, containers of samples, such as sampling containers for blood examinations, testing cells, blood sampling tubes, and sample containers, sterilized containers such as syringes and medical instruments, medical instruments such as beakers, laboratory dishes,

flasks, test tubes, centrifugation tubes, contact lens cases, infusion tubes, piping, joints, and valves, and artificial organs, such as dental plate, artificial heart, non-return valves, and artificial tooth root, and their components;

5 equipments for processing of electronic components, such as wafer carriers, hard disk carriers, information disk substrate carriers, liquid crystal substrate carriers, magnetic disk carriers, IC trays, IC carrier tapes, separation films,

10 shippers, tanks, piping for ultrapure water, pipes, tubes, valves, flowmeters, filters, pumps, sampling containers, resist containers, and inner bags for resist containers; electrical wire

15 coating materials, components for OA equipment, such as electronics, copiers, computers and printers, and general insulators for gauges, radars, antennas, and luminary lamp shades; electric components such as printed boards,

20 flexible printed boards, multilayer printed boards, and high frequency circuit boards; base materials for conductive films; encapsulation materials for transistor, IC, LSI, LED, light diffusion plate, and LED having lenses integrally shaped; sealing

25 materials for electrical components such as motors, capacitors, switches and sensors; housing materials for televisions, videos, video cameras,

and cameras; and building components, such as sewage piping, waterworks piping, pipes, wall covering materials, floor covering materials, and ceiling covering materials.

5 [0063]

[EXAMPLES]

The present invention will be described in further detail by way of the following Examples, but it is to be easily understood that the  
10 invention is not limited to these examples, and various changes and modifications can be made by those skilled in the art within the scope of the invention.

[0064]

15 Example 1 (Synthesis of phenylallyloxymethylstyrene monomer)

$\alpha$ -Bromomethylstyrene (193 g, 1 mol), 262 g (2 mols) of  $\alpha$ -hydroxymethylstyrene, 1,000 ml of dichloromethane, and 15 g of  
20 tetranormalbutylammonium bromide were mixed while cooling in an ice bath. To the mixture, a solution of 140 g (3.5 mols) of sodium hydroxide in 1,000 ml of water was added dropwise. With vigorous stirring, the mixture was reacted for 50  
25 hours, and then the aqueous phase was washed with dichloromethane. Dichloromethane was removed, and the residue was subjected to vacuum distillation



at 140°C and 0.4 mmHg to give 100 g of product A. Since the resulting product was a mixture, it was purified by column chromatography using a hexane/dichloromethane eluent, whereby  
5 phenylallyloxymethylstyrene monomer was obtained.  
[0065]

Example 2 (Synthesis of  
phenylallyloxymethylstyrene polymer 1)

The phenylallyloxymethylstyrene monomer  
10 (100 ml) obtained in Example 1, and 0.006 mol of the polymerization initiator 2,2'-azobisisobutyronitrile (AIBN) were charged into a Pyrex (registered mark) polymerization tube. The polymerization tube was sealed under a nitrogen  
15 atmosphere, or after a freeze-pump-thaw cycle was performed three times, i.e., for 30 minutes, for 40 minutes and for 50 minutes, and the tube was sealed in a vacuum. Then, the reaction mixture was allowed to stand for 24 hours at 60°C in a  
20 temperature-controlled bath to carry out polymerization. The polymerization was stopped by rapidly cooling the polymerization tube with ice. Then, the reaction mixture was poured into methanol as a precipitant to give a polymer as a  
25 white powder. The precipitated polymer was collected by filtration through a glass filter. Methanol was removed, and the residue was dried

for 48 hours or more in a vacuum drying equipment to give phenylallyloxymethylstyrene polymer 1. Based on the ratio between the absorption intensity of phenyl protons and the absorption intensity of pendant olefins, detected by the H-NMR spectrum of the resulting polymer, the degree of cyclization was 90%. The glass transition point (Tg) determined by DSC analysis was 220°C, and the thermal decomposition point determined by TG analysis was 360°C. Moreover, TDS analysis showed the moisture content of this polymer to be 0.008%. The number average molecular weight (Mn) was 14,000.

[0066]

Example 3 (Synthesis of phenylallyloxymethylstyrene polymer 2)

Phenylallyloxymethylstyrene polymer 2 was obtained in the same manner as in Example 2, except that 100 ml of the phenylallyloxymethylstyrene monomer, and 0.006 mol of cumene hydroperoxide (CHP) as a polymerization initiator were charged into the polymerization tube, and the polymerization temperature and the polymerization time were set at 120°C and 24 hours, respectively. The degree of cyclization determined by the H-NMR spectrum of the resulting polymer was 96%. The glass transition point (Tg)

determined by DSC analysis was 250°C, and the thermal decomposition point determined by TG analysis was 380°C. Moreover, TDS analysis showed the moisture content of this polymer to be 0.008%.

5 The number average molecular weight (Mn) was 18,100.

[0067]

#### Example 4 (Synthesis of phenylallyloxymethylstyrene polymer 3)

10 Phenylallyloxymethylstyrene polymer 3 was obtained in the same manner as in Example 2, except that 100 ml of the phenylallyloxymethylstyrene monomer, and 0.006 mol of cumene hydroperoxide (CHP) as a polymerization  
15 initiator were charged into the polymerization tube, and the polymerization temperature and the polymerization time were set at 140°C and 9 hours. The degree of cyclization determined by the H-NMR spectrum of the resulting polymer was 99%. The  
20 glass transition point (Tg) determined by DSC analysis was 265°C, and the thermal decomposition point determined by TG analysis was 400°C. Moreover, TDS analysis showed the moisture content of this polymer to be 0.008%. The number average  
25 molecular weight (Mn) was 12,700.

[0068]

#### Example 5 (Synthesis of allyloxymethylstyrene

monomer)

Allyl bromide (233 g, 1.9 mols), 26 g (0.2 mol) of  $\alpha$ -hydroxymethylstyrene, 1,000 ml of dichloromethane, and 3.4 g (0.01 mol) of tetranormalbutylammonium bromide were mixed with an aqueous sodium hydroxide solution prepared by dissolving 39 g of sodium hydroxide in 290 ml of water. The mixture was heated under reflux for 50 hours at 50°C. After the reaction, the aqueous phase and the organic phase were separated, and the aqueous phase was extracted with ether. Then, the ether phase and the organic phase were mixed, and dried overnight over magnesium sulfate. The desiccant was removed by filtration, and then the ether was removed by distillation. The residue was subjected to vacuum distillation at 54°C and 0.2 mmHg to give 24 g of product B. Since the resulting product contained impurities, it was purified by column chromatography using a cyclohexane/chloroform eluent, whereby allyloxymethylstyrene monomer was obtained.

[0069]

Example 6 (Synthesis of allyloxymethylstyrene polymer 1)

The allyloxymethylstyrene monomer (100 ml) obtained in Example 5, and 0.006 mol of the polymerization initiator 2,2'-

azobisisobutyronitrile (AIBN) were charged into a Pyrex polymerization tube. The polymerization tube was sealed under a nitrogen atmosphere, or after a freeze-pump-thaw cycle was performed three  
5 times, i.e., for 30 minutes, for 40 minutes and for 50 minutes, and the tube was sealed in a vacuum. Then, the reaction mixture was allowed to stand for 24 hours at 60°C in a temperature-controlled bath to carry out polymerization. The  
10 polymerization was stopped by quenching the polymerization tube with ice. Then, the reaction mixture was poured into methanol as a precipitant to give a polymer as a white powder. The precipitated polymer was isolated by filtration  
15 through a glass filter. Methanol was removed, and the residue was dried for 48 hours or more in a vacuum drying equipment to give allyloxymethylstyrene polymer 1. Based on the ratio between the absorption intensity of phenyl  
20 protons and the absorption intensity of pendant olefins, detected by the H-NMR spectrum of the resulting polymer, the degree of cyclization was 88%. The glass transition point (T<sub>g</sub>) determined by DSC analysis was 110°C, and the thermal  
25 decomposition point determined by TG analysis was 350°C. Moreover, TDS analysis showed the moisture content of this polymer to be 0.006%. The number

average molecular weight (Mn) was 5,500.

[0070]

Example 7 (Synthesis of allyloxymethylstyrene polymer 2)

5           Allyloxymethylstyrene polymer 2 was  
obtained in the same manner as in Example 6,  
except that 100 ml of the allyloxymethylstyrene  
monomer, and 0.006 mol of cumene hydroperoxide  
(CHP) as a polymerization initiator were charged  
10 into the polymerization tube, and the  
polymerization temperature and the polymerization  
time were set at 120°C and 24 hours. The degree of  
cyclization determined by the H-NMR spectrum of  
the resulting polymer was 96%. The glass  
15 transition point (Tg) determined by DSC analysis  
was 100°C, and the thermal decomposition point  
determined by TG analysis was 370°C. Moreover, TDS  
analysis showed the moisture content of this  
polymer to be 0.006%. The number average  
20 molecular weight (Mn) was 3,000.

[0071]

Comparative Example 1

          Commercially available thermoplastic  
norbornene-based resin ("ZEON EX280", Zeon  
25 Corporation, Japan) was used as resin, and  
evaluated in the same manner as above. The glass  
transition point (Tg) determined by DSC analysis

was 135°C, and the thermal decomposition point determined by TG analysis was 340°C. Moreover, TDS analysis showed the moisture content of this polymer to be 0.010%.

5 [0072]

#### Comparative Example 2

Commercially available thermoplastic polycarbonate resin ("Panlite AD5503", TEIJIN CHEMICALS LTD., JAPAN) was used as resin, and  
10 evaluated in the same manner as above. The glass transition point (T<sub>g</sub>) determined by DSC analysis was 125°C, and the thermal decomposition point determined by TG analysis was 320°C. Moreover, TDS analysis showed the moisture content of this  
15 polymer to be 0.15%.

[0073]

#### [Evaluation of characteristics]

The results of Examples 2 to 4, Examples 6 and 7, and Comparative Examples 1 to 2 are shown  
20 in Table 1.

[0074]

#### [Table 1]

Synthesis Conditions and Physical Properties of Allyloxymethylstyrene-based resins

	PI	Amount of PI (M)	PTi (h)	PTe (°C)	DC (%)	Tg (°C)	TDP (°C)	MC (%)
Ex. 2	AIBN	0.06	24	60	90	220	360	0.008

Ex. 3	CHP	0.06	24	120	96	250	380	0.008
Ex. 4	CHP	0.02	9	140	99	265	400	0.008
Ex. 6	AIBN	0.06	24	60	88	110	350	0.006
Ex. 7	CHP	0.06	24	120	96	100	370	0.006
C.Ex. 1	-	-	-	-	-	135	340	0.010
C.Ex. 2	-	-	-	-	-	125	320	0.150

[0075]

The thermoplastic phenylallyloxymethylstyrene resins of Examples 2 to 4 according to the present invention are highly heat resistant thermoplastic resins having, as material properties, a very high glass transition point of 220°C or higher and a high thermal decomposition point of 360°C or higher, in comparison with the commercially available thermoplastic resins of Comparative Examples 1 to 2. Compared with conventional thermoplastic injection molding resins, therefore, the resins of the present invention can be molded under high fluidity molding conditions, such as a molding resin temperature of 350°C or higher and a mold temperature of 160°C or higher, as molding conditions, for example, for injection molding. Thus, molded articles with reduced residual stress, minimal surface roughness and few waves can be obtained. Consequently, the resulting molded articles are excellent in shape stability and surface accuracy even when allowed to stand at



high temperatures.

[0076]

On the other hand, the thermoplastic allyloxymethylstyrene resins of Examples 6 to 7 according to the present invention are highly heat resistant thermoplastic resins having, as material properties, a high thermal decomposition point of 350°C or higher, although they have a low glass transition point of 100-110°C, in comparison with the commercially available thermoplastic resins of Comparative Examples 1 to 2. Compared with conventional thermoplastic injection molding resins, therefore, these resins of the present invention can be molded under high fluidity injection molding conditions, such as a molding resin temperature of 340°C or higher, as molding conditions, for example, for injection molding. Thus, molded articles with reduced residual stress, minimal surface roughness and few waves can be obtained. Consequently, the resulting molded articles are excellent in shape stability and surface accuracy even when allowed to stand at high temperatures.

[0077]

Furthermore, the thermoplastic phenylallyloxymethylstyrene resins and the thermoplastic allyloxymethylstyrene resins of

Examples 2 to 4 and 6 to 7 according to the present invention are minimally hygroscopic resins, as compared with the commercially available thermoplastic resins of Comparative Examples 1 to 2. Thus, they can give molded articles which minimally undergo shape changes due to swelling or defect occurrence due to moisture absorption even when allowed to stand at high temperatures.

[0078]

10 [Advantageous Results of the Invention]

According to the allyloxymethylstyrene-based resins of the present invention, there can be provided thermoplastic resins which have a three-dimensional stereochemical rigid structure, and thus retain a high glass transition point (high T<sub>g</sub>) closely related to mechanical strength characteristics, and high thermal stability (high thermal decomposition temperature) permitting high flow molding, and further possess low hygroscopicity meaning minimal swelling, deformation or deterioration due to moisture absorption.

[0079]

Since the thermoplastic allyloxymethylstyrene-based resins of the present invention enable highly accurate, highly reliable molded articles to be produced in large quantities

and at low costs, their commercial value is extremely high.

[DOCUMENT NAME] ABSTRACT

[Abstract]

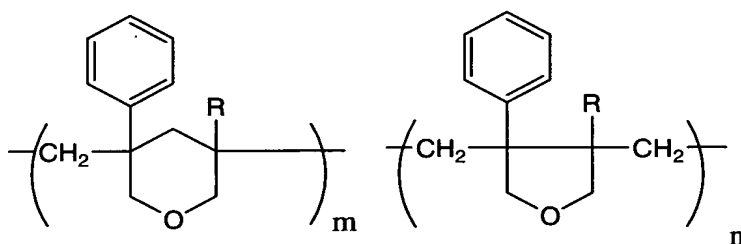
[Problem to Be Solved]

5 A high-performance polymeric material can cope with performance requirements of high performance or high reliability of a product and has a higher stability to heat and a lower hygroscopicity.

[Solving Means]

10 A thermoplastic allyloxymethylstyrene-based resin comprising structural units of the following formulas (I) and (II):

[Chemical Formula 1]



(I)

(II)

15 as repeating units, wherein R represents a hydrogen atom or a hydrocarbon group, and m and n each denote an integer of 0 or 1 or higher, provided that m and n are not 0 at the same time.

20 [Figure Selected]

None

2002-331197

Information on Applicant's Resume

Identification Number [503361248]

1. Date of Change October 2, 2003

[Reason for Change] New Registration

Address: 11-2, Osaki 1-chome, Shinagawa-ku,  
Japan

Name: FUJI ELECTRIC DEVICE TECHNOLOGY CO.,  
LTD.

2003-3109911